

Polyelectrolyte Persistence Length: Attractive Effect of Counterion Correlations and Fluctuations

GIL ARIEL and DAVID ANDELMAN

*School of Physics and Astronomy
Raymond and Beverly Sackler Faculty of Exact Sciences
Tel Aviv University, Tel Aviv 69978, Israel*

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Abstract. –

The persistence length of a single, strongly charged, stiff polyelectrolyte chain is investigated theoretically. Path integral formulation is used to obtain the effective electrostatic interaction between the monomers. We find significant deviations from the classical Odijk, Skolnick and Fixman (OSF) result. An induced attraction between monomers is due to thermal fluctuations and correlations between bound counterions. The electrostatic persistence length is found to be smaller than the OSF value and indicates a possible mechanical instability (collapse) for highly charged polyelectrolytes with multivalent counterions. In addition, we calculate the amount of condensed counterions on a slightly bent polyelectrolyte. More counterions are found to be adsorbed as compared to the Manning condensation on a cylinder.

Polyelectrolytes (PEs) are polymers that have ionizable groups. When dissolved in solution, they dissociate into charged polymer chains and a cloud of free, mobile counterions carrying opposite charges [1, 2]. Such macromolecules appear in numerous industrial applications as well as in biological systems, introducing a new kind of biologically inspired electrostatics [3]. The spatial conformation of a single PE chain has been at the focus of attention of experiments [4, 5], simulations [6, 7] and theoretical models [8, 9, 10, 11, 12, 13], showing a wide range of behavior. The delicate balance between counterion entropy and long range electrostatic repulsion can have opposite effects on different PEs. Broadly speaking, in systems containing weakly charged PEs and monovalent counterions, the electrostatic repulsion dominates and makes the chains stiffer [11, 14]. On the other hand, highly charged PEs with multivalent counterions experience an effective attraction [15] which is not well understood. This attraction leads to enhanced flexibility and, in some cases, induces collapse into a globular conformation [15]. For DNA macromolecules, this is known as DNA condensation [5].

On a mean-field level, the Poisson-Boltzmann (PB) theory predicts only intra-chain repulsion [11]. Another important prediction is the Manning condensation [2, 16], where some of the counterions are loosely bound to the PE chain. Models going beyond mean-field theory take into account correlations and thermal fluctuations [12, 13]. Correlations between bound counterions become more significant at lower temperatures, where the ions are considered to

be arranged in a periodic fashion similar to a Wigner crystal of electronic systems (or a correlated liquid) [12]. At high temperatures, such correlations are smeared out and become less important, while counterion thermal fluctuations get larger and induce an attraction (similar to van der Waals interactions), which competes with the usual repulsion between like charges [13].

Despite an ongoing discussion, there is still no consensus on which of the above mechanisms is more significant in physical situations as realized in experiments [17]. In this letter, we propose a field theoretical approach, which takes into account *both* correlations and thermal fluctuations. This allows a consistent examination of the two contributions at intermediate temperatures and different charge densities of the polymer.

In order to account for counterion condensation we employ a two-phase model [2]: free counterions in solution are in equilibrium with a one-dimensional gas of counterions bound to the polymer backbone. In systems without added salt, the parameter regulating counterion condensation is $q \equiv z l_B / a$ where z is the counterion valency, and e/a is the monomer linear charge density for monomers of size a and charge e . The Bjerrum length is defined as $l_B = e^2 / \epsilon k_B T$, where ϵ is the dielectric constant and $k_B T$ is the thermal energy. We will see that q is the significant (temperature dependent) parameter which determines the system behavior. On an infinite and straight cylinder Manning condensation occurs for $q \geq 1$, and the condensed ions lower the average charge density on the cylinder to an effective $q_{\text{eff}} = 1$ [16]. Below we will show how the condensation picture changes for a semi-flexible PE modeled by a bent cylinder.

We model the polymer as a semi-flexible, worm-like chain of N monomers. The persistence length, $l_p \gg a$, is a measure of the chain flexibility and only the case of a stiff, rod-like polymer, $l_p \gg L \equiv Na$, is considered. It is generally agreed that once condensation is taken into account, the overall charge density on the PE is small, and the effect of free ions is to screen electrostatic interactions [7, 18]. The inverse Debye-Hückel screening length is defined as $\kappa^{-1} = [4\pi z(z+1)l_B c]^{-1/2}$, where c is the concentration of $z : 1$ salt. The screening length is assumed to be much smaller than the polymer contour length, $\kappa^{-1} \ll Na$ (as is usually the case in experiments), and much larger than the monomer size, $\kappa^{-1} \gg a$ (ensuring the validity of the continuum approach employed here). We denote the spatial conformation of the polymer as $\mathbf{R}(s)$, $0 \leq s \leq L$, and the positions along the chain of the I bound counterions as $\mathbf{R}(s_1) \dots \mathbf{R}(s_I)$. Up to a normalization factor, the grand-canonical partition function of the system is

$$\mathcal{Z} = \int \mathcal{D}\mathbf{R}(s) \left(\sum_{I=0}^{\infty} \frac{e^{\mu I}}{I!} \prod_{i=1}^I \frac{1}{L} \int_0^L ds_i \right) e^{-H_0 - H_{\text{int}}}, \quad (1)$$

where the path integral is a sum over all possible spatial conformations of the chain, μ is the chemical potential of a one-dimensional gas of bound counterions, H_0 is the Hamiltonian of a neutral chain with bare persistence length l_0 , and H_{int} is the Hamiltonian of the screened electrostatic interaction between all charged monomers and bound counterions. The monomer charges are assumed to have a uniform charge density e/a along the chain, while the counterions are taken as point-like charges

$$\begin{aligned} H_{\text{int}} &= \frac{1}{2} \int_0^L ds \int_0^L ds' U(\mathbf{R}(s) - \mathbf{R}(s')) \\ &\times \left[z \sum_{i=1}^I \delta(s - s_i) - \frac{1}{a} \right] \left[z \sum_{j=1}^I \delta(s' - s_j) - \frac{1}{a} \right], \end{aligned} \quad (2)$$

where $U(\mathbf{r}) = l_B e^{-\kappa r}/r$ is the screened electrostatic interaction in units of $k_B T$. Because H_{int} of Eq. (2) contains also self-interactions, all following integrations have a lower cut-off at a distance of order a . Continuous concentrations are introduced in the following way

$$\begin{aligned}\phi^{\text{m}}(\mathbf{r}) &= \frac{1}{a} \int_0^L ds \delta(\mathbf{r} - \mathbf{R}(s)) \\ \phi^{\text{b}}(\mathbf{r}) &= \sum_{i=1}^I \delta(\mathbf{r} - \mathbf{R}(s_i)).\end{aligned}\tag{3}$$

These can be substituted into the partition function Eq. (1) by making use of the identity operator which couples the discrete and continuous concentrations. This is done using the path integral representation of the delta function [19,20]. The extra complexity of this method is the introduction of two new auxiliary fields, denoted ψ^{m} and ψ^{b} which couple to ϕ^{m} and ϕ^{b} , respectively. The partition function then reads

$$\begin{aligned}\mathcal{Z} &= \int \mathcal{D}\mathbf{R}(s) \left(\prod_{i=\text{m},\text{b}} \mathcal{D}\phi^i \mathcal{D}\psi^i \xi_i[\mathbf{R}] \right) \exp(-H_{\text{cont}}), \\ \xi_{\text{m}}[\mathbf{R}] &= \exp \left[-H_{\text{id}} + \frac{i}{a} \int_0^L ds \psi^{\text{m}}(\mathbf{R}(s)) \right] \\ \xi_{\text{b}}[\mathbf{R}] &= \exp \left\{ \int d^3\mathbf{r} \left[\frac{e^\mu}{N} e^{i\psi^{\text{b}}(\mathbf{r})} \phi^{\text{m}}(\mathbf{r}) + i\mathbf{\Phi} \cdot \mathbf{\Psi} \right] \right\} \\ H_{\text{cont}} &= \frac{1}{2} \int \int d^3\mathbf{r} d^3\mathbf{r}' \mathbf{\Phi}(\mathbf{r}) \hat{Z} \mathbf{\Phi}(\mathbf{r}') U(\mathbf{r} - \mathbf{r}') \\ \mathbf{\Phi} &= \begin{pmatrix} \phi^{\text{m}} \\ \phi^{\text{b}} \end{pmatrix}, \quad \mathbf{\Psi} = \begin{pmatrix} \psi^{\text{m}} \\ \psi^{\text{b}} \end{pmatrix}, \quad \hat{Z} = \begin{pmatrix} 1 & -z \\ -z & z^2 \end{pmatrix}\end{aligned}\tag{4}$$

where the vectors $\mathbf{\Phi}$ and $\mathbf{\Psi}$ and the matrix \hat{Z} are introduced to simplify notations. Next, ξ_{b} is expanded in powers of ψ^{b} and the integrations over ϕ^{b} and ψ^{b} can be performed. The effective electrostatic interaction H_{eff} and average values of the different fields can be obtained by comparing the partition function of Eq. (4) with that of a neutral system ($e = 0$) [21]. Thus, there is no need to integrate out the polymer degrees of freedom $\{\phi^{\text{m}}\}$ and $\{\psi^{\text{m}}\}$. The method is similar to loop expansion in field theory [19]. The chemical potential μ is set so that at the *straight rod* conformation, the average number of bound counterions per unit length is $n^{\text{M}} = (q - 1)/z^2 l_B = [a^{-1} - (z l_B)^{-1}]/z$, as predicted by Manning [16]. Since the bound counterion phase is in equilibrium with free counterions in solution, μ does not depend on the conformation of the polymer. In our model, as the PE bends, the number of bound counterions is adjusted accordingly in order to maintain this equilibrium.

Fixing the chemical potential of the bound counterion gas, rather than the average density, has greater resemblance to experimental systems, since the ions are only loosely bound and not chemically attached to the polymer. Expanding Eq. (4) to first order in ψ^{b} (this is in fact a Gaussian approximation [21]), μ turns out to be the chemical potential of an *ideal* one-dimensional gas, $\mu = \ln(n^{\text{M}} L)$, and the total charge density does not depend on the conformation of the polymer. The effective interaction Hamiltonian, $H_{\text{eff},1}$ is found to be simply the screened electrostatic interaction between all charges, which are uniformly smeared along the polymer at a constant density, $1/z l_B$.

$$H_{\text{eff},1} = \frac{1}{2z^2 l_B} \int_0^L ds \int_0^L ds' \frac{e^{-\kappa |\mathbf{R}(s) - \mathbf{R}(s')|}}{|\mathbf{R}(s) - \mathbf{R}(s')|}.\tag{5}$$

This is just the Hamiltonian assumed by Odijk, Skolnick and Fixman (OSF) [9,10], and their expression for the persistence length can be easily reproduced

$$l_p = l_0 + l_{\text{OSF}} = l_0 + \frac{1}{4z^2\kappa^2 l_B}, \quad (6)$$

where l_0 is the bare persistence length of the neutral polymer backbone and l_{OSF} is the electrostatic contribution.

Corrections to this approximation are obtained through a cumulant expansion in higher powers of ψ^b . The second order expansion provides a 3-body correction to the effective interaction Hamiltonian [21].

$$H_{\text{eff},2} = -e^\mu \frac{z^2 l_B^2}{2L^3} (N - ze^\mu)^2 \int_0^L \int_0^L \int_0^L ds ds' ds'' \frac{e^{-\kappa|\mathbf{R}(s)-\mathbf{R}(s')|} e^{-\kappa|\mathbf{R}(s)-\mathbf{R}(s'')|}}{|\mathbf{R}(s)-\mathbf{R}(s')| |\mathbf{R}(s)-\mathbf{R}(s'')|} \quad (7)$$

where μ deviates from its ideal gas value and satisfies

$$Ln^M e^{-\mu} = 1 + q(1 - ze^\mu/N) \int_0^L ds \int_0^L ds' \frac{e^{-\kappa|\mathbf{R}(s)-\mathbf{R}(s')|}}{|\mathbf{R}(s)-\mathbf{R}(s')|}. \quad (8)$$

Note that the Manning condensation for an infinite straight cylinder is not expected to change substantially beyond its mean-field value as was discussed in Ref. [22]. Following the method used by Odijk [9], the electrostatic persistence length l_e can now be calculated using the new Hamiltonian, $H_{\text{eff},1} + H_{\text{eff},2}$. For low salt concentrations ($\kappa a \ll 1$), the persistence length can be expanded in powers of $1/\ln \kappa a$ yielding

$$l_e = l_{\text{OSF}} \left[q(2 - q) - \frac{(q - 1)^2}{q \ln(\kappa a)} + O(1/[\ln(\kappa a)]^2) \right]. \quad (9)$$

Equation (9) is our main prediction and is depicted in Fig. 1 for different counterion valencies $z = 1, 2, 3$ as a function of κa . At low salt concentrations ($\kappa a \ll 1$) or high q , the persistence length maintains the OSF κ^{-2} dependence, $l_e \sim l_{\text{OSF}} \sim \kappa^{-2}$. We find that the electrostatic persistence length depends strongly on the valency of the counterions. For monovalent counterions, l_e is usually positive, indicating an effective repulsion between the monomers. However, its value is smaller than the one predicted by OSF. Introduction of multivalent counterions reduces the rigidity of the PE significantly and usually $l_e < 0$, indicating an effective attraction between monomers.

Although the model assumes a rod-like PE, we speculate that a PE mechanical instability can be associated with $l_p = l_0 + l_e = 0$, which represents the limit of validity of rod-like behavior. In Fig. 1 it can be seen that with trivalent counterions, PEs with a wide range of bare persistence lengths, l_0 , will be in a collapsed, globule-like conformation ($l_p < 0$). However, we note that a detailed analysis of the chain mechanical instability requires methods different from the persistence length prescription used in this Letter, to correctly account for the collapse transition.

Using the same method, we performed an expansion to higher orders of ψ^b . Equation (9), valid to second order, accounts for most of the deviation from the OSF result. Third and fourth order terms in the expansion represent only a relatively small correction to the second-order. This point will be discussed in greater detail in a future publication [21]. The expansion

procedure employed here is asymptotic. As such, the approximation improves as higher order terms are taken into account up to a certain order. Beyond this order the expansion diverges.

The leading difference between our l_e and l_{OSF} is through a prefactor which depends on $q(= z l_B/a)$, and which may become negative at large q . The boundary between repulsive (positive) and attractive (negative) electrostatic contributions to the persistence length occurs at $q = 2$, although it is not a true phase transition since the total persistence length $l_p = l_0 + l_e$ is still positive. Taking into account higher order corrections of Eq. (9) may result in a shifted threshold of $q = 2$.

In addition, it is of interest to note that $q = 2$ is the boundary between fluctuation- and correlation-dominated regimes. The length at which the average interaction between bound counterions is equal to $k_B T$ is $z^2 l_B$. This concentration of bound counterions corresponds to $q = 2$. It is expected that for low values of the bound counterion concentration, $1 < q < 2$, where the average electrostatic interaction between ions is smaller than $k_B T$, thermal fluctuations will dominate over the electrostatic, zero temperature ordering. For higher concentrations, $q \gg 2$, models relying on the Wigner crystal picture should be more appropriate. The boundary between the two regimes is at $q = 2$. As attraction is associated with correlations, this comparison gives a new meaning to the $q = 2$ threshold. The two complementary observations show that fluctuations by themselves are not enough to induce effective attraction. This argument, by no means, is a rigorous proof as it does not capture precise numerical prefactors.

It is now possible to compare the persistence length of Eq. (9) with two previous models: one which takes into account thermal fluctuations [13] and another for correlations (correlated liquid) [12]. The comparison with the fluctuation model is rather straightforward. It consists of rewriting Eq. (7) of Ref. [13] in terms of l_{OSF} and q and expanding it in the two limits $q \gg 1$ and $q \gtrsim 1$. In order to compare with the correlation model (at finite κ), we slightly modified the method used by Nguyen et al [12] to account for finite salt concentration. Equation (13) of Ref. [12] describes the interaction of a counterion with a single Wigner-Seitz cell in the absence of added salt. We extend this result in presence of salt by including all cells within a radius κ^{-1} . Then, the obtained expression is expanded in the same two limits. The full derivation will be detailed in a forthcoming, longer paper [21].

For the limit $q \gg 1$ we find that the leading term of the negative electrostatic persistence length of our loop expansion and the correlation model is the same, $l_e \simeq -q^2 l_{\text{OSF}}$. In contrast, the fluctuation model underestimates the electrostatic persistence length, yielding $l_e \simeq l_{\text{OSF}}/q^2$.

For the other limit $q = 1 + \Delta q$, $\Delta q \ll 1$ we find agreement between our model and the thermal fluctuation model [13]: $l_e \simeq l_{\text{OSF}}[1 - O(\Delta q)]$ while the correlation model overestimates it: $l_e \simeq l_{\text{OSF}}[-1 - O(\Delta q)]$. Our expansion qualitatively accounts for both q limits. There are, however, differences in the prefactors.

Furthermore, we note that q , and not just the temperature T , is the relevant parameter which determines the relative contributions of correlations compared to fluctuations. The limits of very low or high temperatures ($\kappa \rightarrow \infty$ or 0 , respectively) are beyond the validity range of our model which explicitly assumes that $L^{-1} \ll \kappa \ll a^{-1}$. Nevertheless, because the leading term of Eq. (9) does not depend on l_B , the electrostatic persistence length l_e neither vanishes nor diverges in these two limits. This shows that the loop expansion method used indeed takes into account both correlations and thermal fluctuations.

Having found the partition function, other thermodynamically averaged quantities can also be obtained. For instance, the density of the bound counterions on a *bent* chain, or alternatively, the effective q . The effective q (q_{eff}) is proportional to the total charge density on the PE chain (monomers and average concentration of bound counterions). To first order

in ψ^b , we find the Manning result: $q_{\text{eff}} = 1$ for all chain conformations. To second order in ψ^b the effective charge density on the chain is smaller

$$q_{\text{eff}} = 1 + (q - 1) \frac{1}{8\kappa^2 \ln \kappa a} \frac{1}{\rho^2} < 1. \quad (10)$$

where ρ is the average cylinder radius of curvature. On a slightly bent rod, the average distance between condensed counterions is smaller and correlations become more significant as compared to the straight-rod case. This makes condensation of counterions more favorable [12]. As the polymer bends, more counterions are able to condense, which in turn drives further reduction of the persistence length. Note that the derivation of Eq. (10) assumes the bending of the chain is only a small perturbation to the straight-rod limit ($\rho \gg L$). On a significantly bent chain ($\rho \sim L$), the situation is completely different, and lies beyond the scope of our model. In the limit of a folded chain resembling a spherical colloidal particle, mean-field theory predicts that counterions are unable to condense at all [2].

In order to examine the effect of the increased condensation, we look at the asymptotic form of Eq. (9) for $q = 1 + \Delta q$, $\Delta q \ll 1$ in two cases. In the first we allow the density of the bound counterions to be adjusted according to the equilibrium condition with the bulk (this is an expansion of Eq. (9) in Δq). In the second case we add a constraint that fixes the density to be according to Manning for all conformations of the polymer. Expanding in Δq we recalculate l_e for both cases

$$\begin{aligned} l_e &= l_{\text{OSF}} [1 + \mathcal{O}(\Delta q^2)] \\ l_e^{\text{fixed}} &= l_{\text{OSF}} [1 - [1/\ln(\kappa a)]\Delta q + \mathcal{O}(\Delta q^2)]. \end{aligned} \quad (11)$$

The persistence length is highly sensitive to the density of the multivalent counterions. Comparison between the above two expressions shows that corrections to Manning condensation for bent polymer chains have a substantial influence on the persistence length.

In conclusion, we have derived an expression for the electrostatic persistence length of a single, stiff, strongly charged PE, taking into account both correlations and thermal fluctuations of the bound counterions. Correlations dominate for $q \gg 1$, whereas thermal fluctuations for $q \gtrsim 1$. These two mechanisms were considered separately in Ref. [12] and Ref. [13], respectively. The advantage of our loop expansion method is that it takes both mechanisms into account. As a result, it covers a large range of counterion valencies and polymer charge densities and offers a possible explanation for the discrepancies between the two models.

Our results show a considerable decrease in the polymer stiffness (via its persistence length) for systems with multivalent counterions, $z \geq 2$. This decrease depends on the modified Manning-Oosawa parameter q . The estimates obtained for the collapse of semi-flexible PEs in presence of multivalent counterions are reasonable and are related, at least qualitatively, to the phenomenon of DNA condensation. The effective Hamiltonian of Eq. (7) has the form of a three-body interaction. In the current model this is the main source of attraction and can explain the high sensitivity of the chain rigidity to the counterion valency z .

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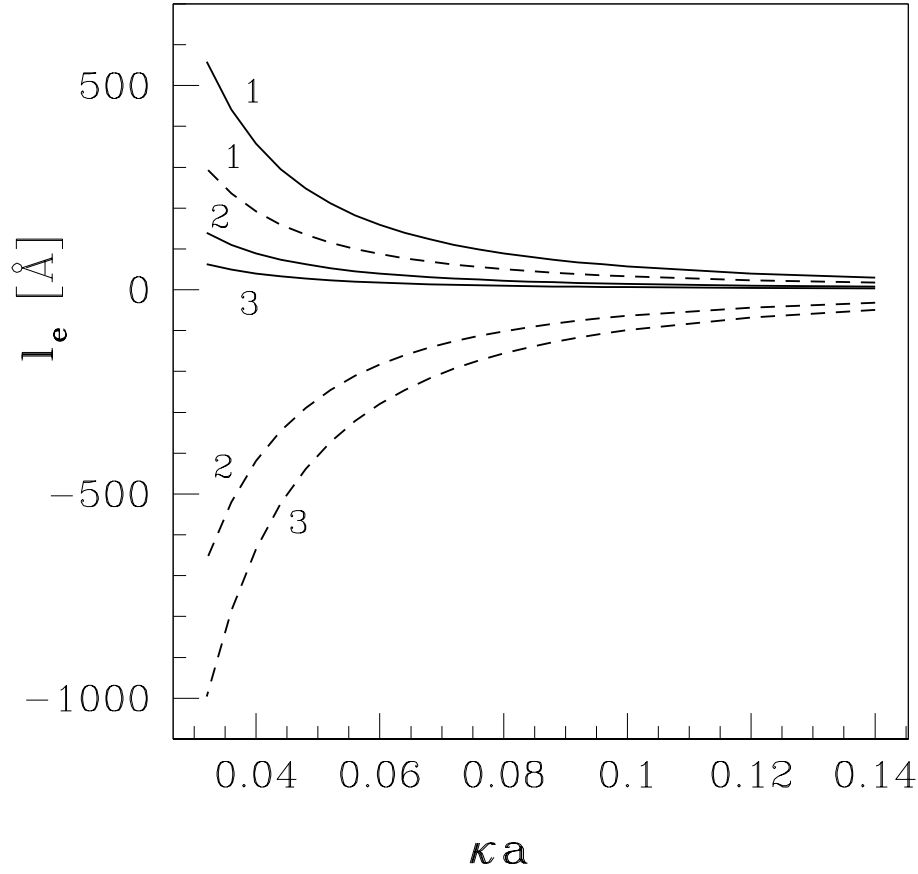


Fig. 1 – The electrostatic persistence length l_e as function of κa according to OSF (solid line) and our Eq. (9) (dashed line). Valencies are specified next to each curve. The parameters chosen are: $a = 4 \text{ \AA}$, $l_B = 7 \text{ \AA}$, so that $q = 1.75z$. The negative l_e values for $z = 2, 3$ indicate a possible collapse transition of the PE chain.